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STEEL - MAKING SLAG AS CATALYST FOR DRY REFORMING OF CH_4

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Abstract

The use of steel-making slag as catalysts for microwave-assisted dry reforming of CH_4 was studied. Carbon materials (an activated carbon and a metallurgical coke), mixtures of carbon materials + Fe-rich slag and mixtures of carbon materials + Ni/Al_2O_3 were tested as catalysts. Mixtures of slag with carbons gave rise to higher and steadier conversions than those achieved over carbon materials. The case of mixtures with metallurgical coke was remarkably, changing from no conversion when coke was used alone to high values when it was mixed with metal-rich catalysts.

Keywords: Steel-making slag, Carbon catalyst, Dry reforming, Microwave heating

INTRODUCTION

In recent years, the process of dry reforming (reaction 1) has been proposed as a promising technology, not only because syngas is produced with adequate H_2/CO ratio for the production of liquid hydrocarbons but also because methane and carbon dioxide, both greenhouse gases, are converted into valuable feedstock [1].

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \qquad (1)$$

One of the major obstacles for the industrial application of this technology is that no effective catalyst exists, due to deactivation because of the carbon deposition. Numerous attempts have been made to develop catalysts for this reaction; the most efficient are based on noble metals. Nevertheless, Ni-based catalysts are preferred since are cheaper than noble metal based catalysts and exhibit high activity for dry reforming reaction with moderate resistance to carbon deposits [2]. Besides, other conventional metal-based catalysts have been evaluated. Regarding Fe catalysts, they show poorer activity and selectivity [3]. However, substitution of Ni by low contents of Fe (i.e. Ni-Fe catalysts) promotes more stable catalysts [4].

The use of carbon materials as catalysts has also been proposed [5, 6], including chars from biomass residues [7]. Carbon-based catalysts offer some advantages over metal catalysts as availability, durability and low cost. Besides, the good ability of carbons in absorption of microwaves makes them adequate catalysts for microwave-assisted dry reforming, an alternative method of heating that enhances heterogeneous and heterogeneous catalytic reactions [6, 7].

The aim of this work is to study the catalytic activity of steel slag, a Fe-rich waste material produced during the process of steel making, in the microwave-assisted dry reforming of CH_4. In order to compare the performance of this residue, alternative carbon catalysts and conventional Ni-based catalyst are also studied.

EXPERIMENTAL

Microwave-assisted CO_2 reforming of CH_4 was carried out using as catalyst a physical mixture of Fe-rich steel-making slag (eFe, with 15.2 wt. % of Fe content) with a carbonaceous material (an activated carbon, FY5, or a metallurgical coke, CQ) in a proportion 1:1 (wt.%). In order to evaluate the performance as catalyst of this residue, mixtures of carbon material with an in-lab prepared catalyst of Ni/Al_2O_3 (5 wt. % of Ni content) were also tested.

Experiments were conducted in a quartz reactor charged with 6 g of catalyst, previously dried overnight at 100 ºC, and heated up to 800 ºC in a single mode microwave oven (MW). Details of this equipment setup have been described elsewhere [6]. Experiments were carried out in three steps of 180 min, according to the flow conditions and

requirements described in the protocol shown in Figure 1.

Produced gases were analyzed in a Varian CP-3800 gas-chromatograph equipped with a TCD detector. Concentrations in the effluent gas were used for calculating the conversions of CH_4 and CO_2:

CH_4 conversion, % = 100 x $[(H_2)_{out}/2]/[(CH_4)_{out}+(H_2)_{out}/2]$

CO_2 conversion, % = 100 x $[(CO)_{out}/2]/[(CO_2)_{out}+(CO)_{out}/2]$

RESULTS AND DISCUSSION

Preliminary heating tests of steel-making slag (eFe) showed that this residue does not absorb microwave energy, i.e. steel slag is not a microwave receptor. Therefore, it must be mixed with an absorber material (in the present work, a carbonaceous material) in order to be used as catalyst for the microwave-assisted dry reforming reaction.

Conversions over FY5, CQ, and mixtures of FY5 + eFe and CQ + eFe are shown in Figure 2 and 3, respectively. CO_2 and CH_4 conversions can be very different depending on the carbon material used as catalyst [5]. Thus, FY5, which has a large micropores volume, gave rise to high initial conversions followed by a rapid drop of conversion, especially in the case of CH_4 [6], whereas metallurgical coke CQ, with no textural development, was found to be a poor catalyst for dry reforming reaction. As can be seen, mixtures of carbon + eFe were better catalysts. Interestingly, mixture of slag and coke (CQ + eFe) gave rise to moderate but steady conversion (discarding first points), improving not only CH_4 conversion but also CO_2 conversion regarding 100% of CQ.

In the case of FY5 + eFe, steady conversions were also obtained, avoiding the fast deactivation observed over FY5. Therefore, addition of Fe-rich slag improved the activity of the catalytic mixtures. Nevertheless, the type of carbon material used influence notably on the performance of the mixture, FY5 + eFe being better, which shows that carbon materials not only acted as mere microwave receptors but also as catalysts.

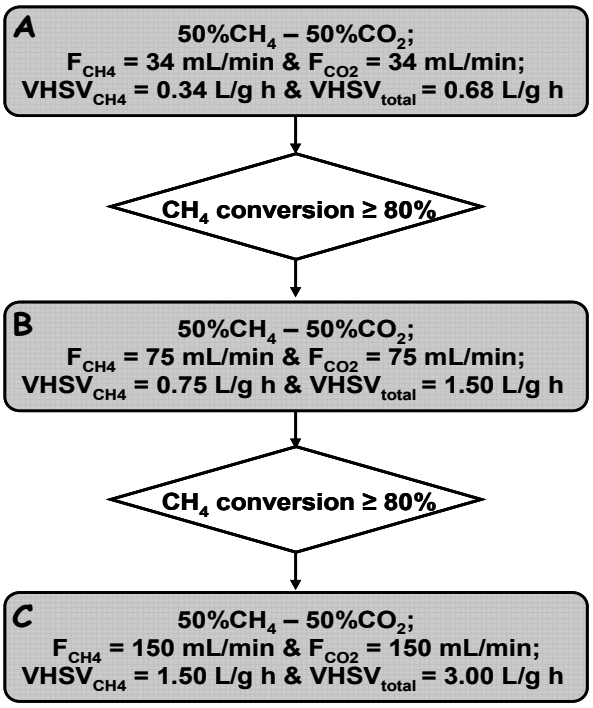

Figure 1. Protocol followed in the evaluation of different mixtures metal-rich phase + carbonaceous material used as catalysts in the dry reforming reaction.

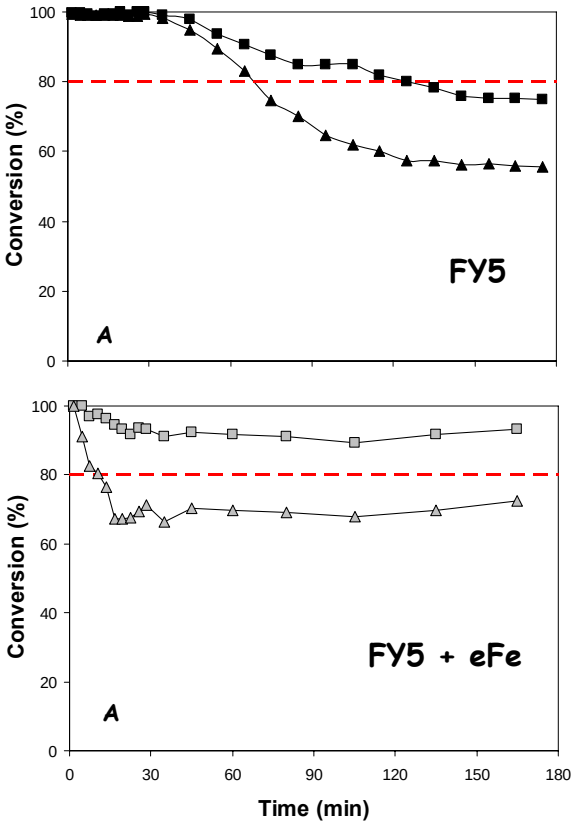

Figure 2. CO_2 (square symbol) and CH_4 (triangle symbol) conversions for dry reforming reaction carried out over activated carbon (FY5) and the mixture of activated carbon and steel making slag (FY5 + eFe).

In order to check the catalytic activity of steel-making slag, mixtures of carbon + eFe were compared with mixtures of carbon + Ni/Al_2O_3 (in-lab prepared catalyst). As it was expected, mixtures of carbon material + Ni/Al_2O_3 were better catalysts than mixtures with eFe. Thus, by using these catalysts it is possible to maintain conversions near to 100%, increasing about six times the $VHSV_{total}$ used, regarding carbons and mixtures with eFe (see Figure 4).

It can be observed that conversions over mixtures with FY5 were again higher than over mixtures with CQ. Nevertheless, improvement in catalytic activity was much more significant for CQ, changing from no CH_4 conversion to about 80%, even after increasing $VHSV_{total}$. This result shows that residual fractions of metallurgical coke could be used as catalysts/microwave receptors for dry reforming.

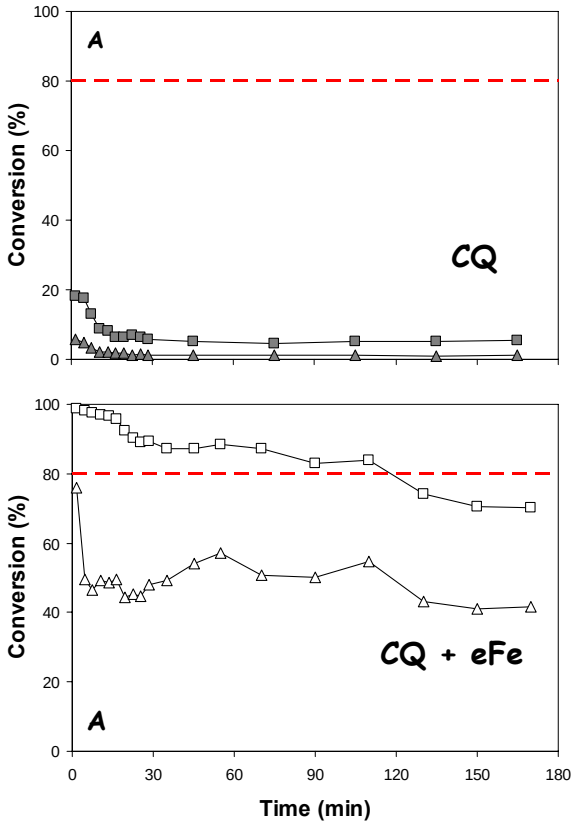

Figure 3. CO_2 (square symbol) and CH_4 (triangle symbol) conversion for dry reforming reaction carried out over coke (CQ) and the mixture of coke and steel making slag (CQ + eFe).

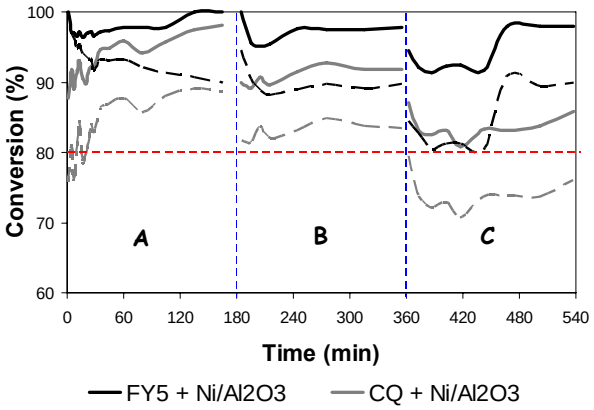

Figure 4. CO_2 (solid lines) and CH_4 (doted lines) conversions for dry reforming reaction carried out over mixtures of two different carbon materials and an in-lab prepared Ni-based catalyst: FY5 + Ni/Al_2O_3; CQ + Ni/Al_2O_3.

CONCLUSIONS

Steel-making slag can be used as catalyst for microwave-assisted dry reforming. However, they must be mixed with a microwave absorber, i.e a carbon material, since slag is not an absorber and therefore it does not heat in the microwave oven. Conversions achieved using a mixture 1:1 of carbon material + Fe-rich slag are found to be steadier than conversions obtained over carbon alone. Besides, catalytic activity of mixtures depends on the carbon material selected. Thus, higher conversions are achieved using an activated carbon, which is better catalyst than a metallurgical coke when only carbon material is used. Nevertheless, the activity of metallurgical coke is dramatically improved when a metal-rich fraction is added, specially mixed with Ni-based catalyst. Actually, mixtures of carbon materials with Ni/Al_2O_3 give rise to higher conversions than mixtures with slag, allowing $VHSV_{total}$ to be increased while high conversions are kept.

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